

WE CLAIM:

-1-

A process for producing an aminoarylboronic ester which comprises:

(a) reacting an aryl compound with a borane selected from the group consisting of a borane with a
5 B-H, B-B, and B-Si bond in the presence of a catalytically effective amount of an iridium or rhodium complex with three or more substituents, and an organic ligand selected from the group consisting of phosphorus, carbon, nitrogen, oxygen, and sulfur
10 organic ligands under anhydrous conditions to produce an arylboronic ester; and

(b) aminating the arylboronic ester with an organic compound containing an amine moiety in the presence of a catalytically effective amount of a
15 metal catalyst complex under anhydrous conditions wherein the organic compound is coupled to the aryl group of the arylboronic ester compound to produce the aminoarylboronic ester.

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The process of Claim 1 wherein the iridium complex is selected from the group consisting of

$((\text{COD})\text{Ir}(\text{OCH}_3))_2$, $(\text{Cp}^*)\text{Ir}(\text{H})_2(\text{Me}_3\text{P})$,
 $(\text{Cp}^*)\text{Ir}(\text{H})(\text{BPin})(\text{Me}_3\text{P})$, $(\text{Cp}^*)\text{Ir}(\text{H})(\text{C}_6\text{H}_5)(\text{Me}_3\text{P})$,
5 $(\text{Ind})\text{Ir}(\text{COD})$, $(\text{Ind})\text{Ir}(\text{dppe})$, $(\text{MesH})\text{Ir}(\text{BPin})(\text{B}(\text{OR})_2)_2$,
 $((\text{R}_1)_3\text{P})_3\text{Ir}(\text{B}(\text{OR}_2)_2)_3$, $(\text{R}_1)_2\text{P})_2\text{Ir}(\text{BPin})_3$,
 $((\text{R}_1)_2\text{P})_3\text{Ir}((\text{R}_2\text{O})_2\text{B})_3)_2$, $((\text{R}_1)_3\text{P})_4\text{Ir}(\text{BPin})$,
 $((\text{R}_1)_3\text{P})_2\text{Ir}(\text{BPin})_3$, $(\text{MesH})\text{Ir}(\text{BPin})_3$, and $(\text{IrCl}(\text{COD}))_2$,
 $(\text{PMe}_3)_2\text{IrH}_5$, $((\text{R}_1)_3\text{P})_2\text{IrH}_5$, and $((\text{R})_3\text{P})_2\text{IrH}_x(\text{B}(\text{OR}_2)_2)_{5-x}$
10 where x is 0-4, wherein Cp^* is 1,2,3,4,5-pentamethylcyclopentadienyl, BPin is pinacolborane, Me is methyl, H is hydrogen, P is phosphorus, Ind is indenyl, COD is 1,5-cyclooctadiene, MesH is mesitylene, and wherein R, R_1 , and R_2 are hydrogen,
15 linear or branched alkyl containing 1 to 8 carbons, aryl, or a carbon in a cyclic structure.

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The process of Claim 1 wherein the iridium complex is $(\text{Ind})\text{Ir}(\text{COD})$ wherein Ind is indenyl and COD is 1,5-cyclooctadiene.

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The process of Claim 1 wherein the iridium complex is $((\text{COD})\text{Ir}(\text{OCH}_3))_2$ wherein COD is 1,5-cyclooctadiene.

-5-

The process of Claim 1 wherein the organic ligand is a phosphorus organic ligand selected from the group consisting of trimethyl phosphine (PMe_3), 1,2-bis(dimethylphosphino)ethane (dmpe), and 1,2-
5 bis(diphenylphosphino)ethane (dppe).

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The process of Claim 1 wherein the organic ligand is a nitrogen ligand selected from the group consisting of 2,2'-dipyridyl and 4,4'-di-tert-butyl-2,2'-dipyridyl.

-7-

The process of Claim 1 wherein the borane is pinacolborane (BPin).

-8-

The process of Claim 1 wherein the metal catalyst is palladium.

-9-

The process of Claim 1 wherein the metal catalyst complex is selected from the group consisting of $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}_2(\text{dba})_3$, $\text{Pd}_2(\text{dba})_3/\text{P}(\text{tBu})_3$, $\text{PdCl}_2(\text{dppf})$, and $\text{Pd}(\text{OAc})_2/\text{Cy}_3\text{P}$ wherein P is phosphorus and Ph is
5 phenyl, dba is dibenzylideneacetone, tBu is *tert*-butyl, dppf is diphenylphosphinoferrocene.

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The process of Claim 1 wherein the aryl compound has the formula $(\text{R})\text{Ar}(\text{X})$, the arylboronic ester has the formula $(\text{R})\text{Ar}(\text{X})\text{B}(\text{OR}_1)$, and the aminoarylboronic ester has the formula
5 $(\text{R})\text{Ar}(\text{NR}_2\text{R}_3)\text{B}(\text{OR}_1)_2$ wherein R, R_2 , and R_3 are each selected from the group consisting of alkyl, aryl, vinyl, alkoxy, carboxylic esters, amides, and halogen; Ar is selected from the group consisting of phenyl, naphthyl, anthracyl, and heteroaryl; X is selected
10 from the group consisting of chloro, bromo, iodo, triflates, and nonaflates; and R_1 is selected from the group consisting of alkyl, hydrogen, and aryl.

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The process of Claim 1 wherein the aminoarylboronic ester is reacted with an oxidizing compound to remove the boronic ester group.

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The process of Claim 1 wherein the molar ratio of the aryl compound to the borane is between about 10 to 1 and 1 to 10.

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The process of Claim 1 wherein the molar ratio of the aryl compound to borane is about 1 to 2.

-14-

The process of Claim 1 wherein the amination includes a base and a second organic ligand.

-15-

The process of Claim 14 wherein the base is K_3PO_4 .

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The process of Claim 14 wherein the second organic ligand is selected from the group consisting of $PtBu_3$, 2-(N,N'-dimethylamino)-2'-dicyclophosphino-1,1'-biphenyl, 2-dicyclohexylphosphino-1,1'-biphenyl,
5 and 2-di-t-butylphosphino-1,1'-biphenyl.

A process for producing an aminoarylboronic ester which comprises:

(a) reacting in a reaction vessel an aryl compound with a borane selected from the group consisting of a borane with a B-H, B-B, and B-Si bond in the presence of a catalytically effective amount of an iridium or rhodium complex with three or more substituents, and an organic ligand selected from the group consisting of phosphorus, carbon, nitrogen, oxygen, and sulfur organic ligands under anhydrous conditions to produce an arylboronic ester; and

(b) aminating the arylboronic ester formed in the reaction vessel with an organic compound containing an amine moiety in the presence of a catalytically effective amount of a metal catalyst complex under anhydrous conditions wherein the organic compound is coupled to the aryl group of the arylboronic ester compound to produce the aminoarylboronic ester.

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The process of Claim 17 wherein the iridium complex is selected from the group consisting of

- $((\text{COD})\text{Ir}(\text{OCH}_3))_2$, $(\text{Cp}^*)\text{Ir}(\text{H})_2(\text{Me}_3\text{P})$,
 $(\text{Cp}^*)\text{Ir}(\text{H})(\text{BPin})(\text{Me}_3\text{P})$, $(\text{Cp}^*)\text{Ir}(\text{H})(\text{C}_6\text{H}_5)(\text{Me}_3\text{P})$,
5 $(\text{Ind})\text{Ir}(\text{COD})$, $(\text{Ind})\text{Ir}(\text{dppe})$, $(\text{MesH})\text{Ir}(\text{BPin})(\text{B}(\text{OR})_2)_2$,
 $((\text{R}_1)_3\text{P})_3\text{Ir}(\text{B}(\text{OR}_2)_2)_3$, $(\text{R}_1)_2\text{P})_2\text{Ir}(\text{BPin})_3$,
 $((\text{R}_1)_2\text{P})_3\text{Ir}((\text{R}_2\text{O})_2\text{B})_3)_2$, $((\text{R}_1)_3\text{P})_4\text{Ir}(\text{BPin})$,
 $((\text{R}_1)_3\text{P})_2\text{Ir}(\text{BPin})_3$, $(\text{MesH})\text{Ir}(\text{BPin})_3$, and $(\text{IrCl}(\text{COD}))_2$,
 $(\text{PMe}_3)_2\text{IrH}_5$, $((\text{R}_1)_3\text{P})_2\text{IrH}_5$, and $((\text{R})_3\text{P})_2\text{IrH}_x(\text{B}(\text{OR}_2)_2)_{5-x}$
10 where x is 0-4, wherein Cp^* is 1,2,3,4,5-pentamethylcyclopentadienyl, BPin is pinacolborane, Me is methyl, H is hydrogen, P is phosphorus, Ind is indenyl, COD is 1,5-cyclooctadiene, MesH is mesitylene, and wherein R, R_1 , and R_2 are hydrogen,
15 linear or branched alkyl containing 1 to 8 carbons, aryl, or a carbon in a cyclic structure.

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The process of Claim 17 wherein the iridium complex is $(\text{Ind})\text{Ir}(\text{COD})$ wherein Ind is indenyl and COD is 1,5-cyclooctadiene.

-20-

The process of Claim 17 wherein the iridium complex is $((\text{COD})\text{Ir}(\text{OCH}_3))_2$ wherein COD is 1,5-cyclooctadiene.

-21-

The process of Claim 17 wherein the organic ligand is a phosphorus organic ligand selected from the group consisting of trimethyl phosphine (PMe_3), 1,2-bis(dimethylphosphino)ethane (dmpe), and 1,2-bis(diphenylphosphino)ethane (dppe).

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The process of Claim 17 wherein the organic ligand is a nitrogen ligand selected from the group consisting of 2,2'-dipyridyl and 4,4'-di-tert-butyl-2,2'-dipyridyl.

-23-

The process of Claim 17 wherein the borane is pinacolborane (BPin).

-24-

The process of Claim 17 wherein the metal catalyst is palladium.

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The process of Claim 17 wherein the metal catalyst complex is selected from the group consisting of $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}_2(\text{dba})_3$, $\text{Pd}_2(\text{dba})_3/\text{P}(\text{tBu})_3$, $\text{PdCl}_2(\text{dppf})$, and $\text{Pd}(\text{OAc})_2/\text{Cy}_3\text{P}$ wherein P is phosphorus and Ph is phenyl, dba is dibenzylideneacetone, tBu is tert-butyl, dppf is diphenylphosphinoferrocene.

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The process of Claim 17 wherein the aryl compound has the formula $(R)Ar(X)$, the arylboronic ester has the formula $(R)Ar(X)B(OR_1)$, and the aminoarylboronic ester has the formula
5 $(R)Ar(NR_2R_3)B(OR_1)_2$ wherein R, R_2 , and R_3 are each selected from the group consisting of alkyl, aryl, vinyl, alkoxy, carboxylic esters, amides, and halogen; Ar is selected from the group consisting of phenyl, naphthyl, anthracyl, and heteroaryl; X is selected
10 from the group consisting of chloro, bromo, iodo, triflates, and nonaflates; and R_1 is selected from the group consisting of alkyl, hydrogen, and aryl.

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The process of Claim 17 wherein the aminoarylboronic ester is reacted with an oxidizing compound to replace the boronic ester group with oxygen.

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The process of Claim 17 wherein the molar ratio of the aryl compound to the borane is between about 10 to 1 and 1 to 10.

-29-

The process of Claim 17 wherein the molar ratio of the aryl compound to borane is about 1 to 2.

-30-

The process of Claim 17 wherein the amination includes a base and a second organic ligand.

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The process of Claim 30 wherein the base is K_3PO_4 .

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The process of Claim 30 wherein the second organic ligand is selected from the group consisting of $PtBu_3$, 2-(N,N'-dimethylamino)-2'-dicyclophosphino-1,1'-biphenyl, 2-dicyclohexylphosphino-1,1'-biphenyl, and 2-di-t-butylphosphino-1,1'-bipheyl.

A process for C-N coupling an aryl halide to an aminoarylboronic ester via the amine functionality of the aminoarylboronic ester which comprises:

(a) reacting in a reaction vessel an aryl
5 compound with a borane selected from the group consisting of a borane with a B-H, B-B, and B-Si bond in the presence of a catalytically effective amount of an iridium or rhodium complex with three or more substituents, and an organic ligand selected from the
10 group consisting of phosphorus, carbon, nitrogen, oxygen, and sulfur organic ligands under anhydrous conditions to produce an arylboronic ester;

(b) aminating the arylboronic ester formed in the reaction vessel with an organic compound
15 containing an amine moiety in the presence of a catalytically effective amount of a metal catalyst complex under anhydrous conditions wherein the organic compound is coupled to the aryl group of the arylboronic ester compound to produce the
20 aminoarylboronic ester; and

(c) reacting the aminoarylboronic ester with the aryl halide in the presence of a palladium metal catalyst complex under anhydrous conditions to couple the aryl halide to the amine functionality of the
25 aminoarylboronic ester.

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The process of Claim 33 wherein the iridium complex is selected from the group consisting of

$((\text{COD})\text{Ir}(\text{OCH}_3))_2$, $(\text{Cp}^*)\text{Ir}(\text{H})_2(\text{Me}_3\text{P})$,
 $(\text{Cp}^*)\text{Ir}(\text{H})(\text{BPin})(\text{Me}_3\text{P})$, $(\text{Cp}^*)\text{Ir}(\text{H})(\text{C}_6\text{H}_5)(\text{Me}_3\text{P})$,
5 $(\text{Ind})\text{Ir}(\text{COD})$, $(\text{Ind})\text{Ir}(\text{dppe})$, $(\text{MesH})\text{Ir}(\text{BPin})(\text{B}(\text{OR})_2)_2$,
 $((\text{R}_1)_3\text{P})_3\text{Ir}(\text{B}(\text{OR}_2)_2)_3$, $(\text{R}_1)_2\text{P})_2\text{Ir}(\text{BPin})_3$,
 $((\text{R}_1)_2\text{P})_3\text{Ir}((\text{R}_2\text{O})_2\text{B})_3)_2$, $((\text{R}_1)_3\text{P})_4\text{Ir}(\text{BPin})$,
 $((\text{R}_1)_3\text{P})_2\text{Ir}(\text{BPin})_3$, $(\text{MesH})\text{Ir}(\text{BPin})_3$, and $(\text{IrCl}(\text{COD}))_2$,
 $(\text{PMe}_3)_2\text{IrH}_5$, $((\text{R}_1)_3\text{P})_2\text{IrH}_5$, and $((\text{R})_3\text{P})_2\text{IrH}_x(\text{B}(\text{OR}_2)_2)_{5-x}$
10 where x is 0-4, wherein Cp^* is 1,2,3,4,5-pentamethylcyclopentadienyl, BPin is pinacolborane, Me is methyl, H is hydrogen, P is phosphorus, Ind is indenyl, COD is 1,5-cyclooctadiene, MesH is mesitylene, and wherein R, R_1 , and R_2 are hydrogen,
15 linear or branched alkyl containing 1 to 8 carbons, aryl, or a carbon in a cyclic structure.

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The process of Claim 33 wherein the iridium complex is $(\text{Ind})\text{Ir}(\text{COD})$ wherein Ind is indenyl and COD is 1,5-cyclooctadiene.

-36-

The process of Claim 33 wherein the iridium complex is $((\text{COD})\text{Ir}(\text{OCH}_3))_2$ wherein COD is 1,5-cyclooctadiene.

-37-

The process of Claim 33 wherein the organic ligand is a phosphorus organic ligand selected from the group consisting of trimethyl phosphine (PMe_3), 1,2-bis(dimethylphosphino)ethane (dmpe), and 1,2-bis(diphenylphosphino)ethane (dppe).

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The process of Claim 33 wherein the organic ligand is a nitrogen ligand selected from the group consisting of 2,2'-dipyridyl and 4,4'-di-tert-butyl-2,2'-dipyridyl.

-39-

The process of Claim 33 wherein the borane is pinacolborane (BPin).

-40-

The process of Claim 33 wherein the metal catalyst is palladium.

-41-

The process of Claim 33 wherein the metal catalyst complex is selected from the group consisting of $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}_2(\text{dba})_3$, $\text{Pd}_2(\text{dba})_3/\text{P}(\text{tBu})_3$, $\text{PdCl}_2(\text{dppf})$, and $\text{Pd}(\text{OAc})_2/\text{Cy}_3\text{P}$ wherein P is phosphorus and Ph is phenyl, dba is dibenzylideneacetone, tBu is tert-butyl, dppf is diphenylphosphinoferrocene.

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The process of Claim 33 wherein the aryl compound has the formula $(R)Ar(X)$, the arylboronic ester has the formula $(R)Ar(X)B(OR_1)$, and the aminoarylboronic ester has the formula
5 $(R)Ar(NR_2R_3)B(OR_1)_2$ wherein R, R_2 , and R_3 are each selected from the group consisting of alkyl, aryl, vinyl, alkoxy, carboxylic esters, amides, and halogen; Ar is selected from the group consisting of phenyl, naphthyl, anthracyl, and heteroaryl; X is selected
10 from the group consisting of chloro, bromo, iodo, triflates, and nonaflates; and R_1 is selected from the group consisting of alkyl, hydrogen, and aryl.

-43-

The process of Claim 33 wherein the molar ratio of the aryl compound to the borane is between about 10 to 1 and 1 to 10.

-44-

The process of Claim 33 wherein the molar ratio of the aryl compound to borane is about 1 to 2.

-45-

The process of Claim 33 wherein the amination includes a base and a second organic ligand.

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The process of Claim 45 wherein the base is K_3PO_4 .

The process of Claim 45 wherein the second organic ligand is selected from the group consisting of PtBu_3 , 2-(N,N'-dimethylamino)-2'-dicyclophosphino-1,1'-biphenyl, 2-dicyclohexylphosphino-1,1'-biphenyl, and 2-di-t-butylphosphino-1,1'-biphenyl.

A process for C-C coupling an aryl halide to an aminoarylboronic ester via the borane functionality of the aminoarylboronic ester which comprises:

(a) reacting in a reaction vessel an aryl compound with a borane selected from the group consisting of a borane with a B-H, B-B, and B-Si bond in the presence of a catalytically effective amount of an iridium or rhodium complex with three or more substituents, and an organic ligand selected from the group consisting of phosphorus, carbon, nitrogen, oxygen, and sulfur organic ligands under anhydrous conditions to produce an arylboronic ester;

(b) aminating the arylboronic ester formed in the reaction vessel with an organic compound containing an amine moiety in the presence of a catalytically effective amount of a metal catalyst complex under anhydrous conditions wherein the organic compound is coupled to the aryl group of the arylboronic ester compound to produce the aminoarylboronic ester; and

(c) reacting the aminoarylboronic ester with the aryl halide in the presence of a palladium metal catalyst complex in the presence of water to couple the aryl halide to the aminoarylboronic ester.

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The process of Claim 48 wherein the iridium complex is selected from the group consisting of

$((\text{COD})\text{Ir}(\text{OCH}_3))_2$, $(\text{Cp}^*)\text{Ir}(\text{H})_2(\text{Me}_3\text{P})$,
 $(\text{Cp}^*)\text{Ir}(\text{H})(\text{BPin})(\text{Me}_3\text{P})$, $(\text{Cp}^*)\text{Ir}(\text{H})(\text{C}_6\text{H}_5)(\text{Me}_3\text{P})$,
5 $(\text{Ind})\text{Ir}(\text{COD})$, $(\text{Ind})\text{Ir}(\text{dppe})$, $(\text{MesH})\text{Ir}(\text{BPin})(\text{B}(\text{OR})_2)_2$,
 $((\text{R}_1)_3\text{P})_3\text{Ir}(\text{B}(\text{OR}_2)_2)_3$, $(\text{R}_1)_2\text{P})_2\text{Ir}(\text{BPin})_3$,
 $((\text{R}_1)_2\text{P})_3\text{Ir}((\text{R}_2\text{O})_2\text{B})_3)_2$, $((\text{R}_1)_3\text{P})_4\text{Ir}(\text{BPin})$,
 $((\text{R}_1)_3\text{P})_2\text{Ir}(\text{BPin})_3$, $(\text{MesH})\text{Ir}(\text{BPin})_3$, and $(\text{IrCl}(\text{COD}))_2$,
 $(\text{PMe}_3)_2\text{IrH}_5$, $((\text{R}_1)_3\text{P})_2\text{IrH}_5$, and $((\text{R})_3\text{P})_2\text{IrH}_x(\text{B}(\text{OR}_2)_2)_{5-x}$
10 where x is 0-4, wherein Cp^* is 1,2,3,4,5-pentamethylcyclopentadienyl, BPin is pinacolborane, Me is methyl, H is hydrogen, P is phosphorus, Ind is indenyl, COD is 1,5-cyclooctadiene, MesH is mesitylene, and wherein R, R_1 , and R_2 are hydrogen,
15 linear or branched alkyl containing 1 to 8 carbons, aryl, or a carbon in a cyclic structure.

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The process of Claim 48 wherein the iridium complex is $(\text{Ind})\text{Ir}(\text{COD})$ wherein Ind is indenyl and COD is 1,5-cyclooctadiene.

-51-

The process of Claim 48 wherein the iridium complex is $((\text{COD})\text{Ir}(\text{OCH}_3))_2$ wherein COD is 1,5-cyclooctadiene.

-52-

The process of Claim 48 wherein the organic ligand is a phosphorus organic ligand selected from the group consisting of trimethyl phosphine (PMe_3), 1,2-bis(dimethylphosphino)ethane (dmpe), and 1,2-bis(diphenylphosphino)ethane (dppe).

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The process of Claim 48 wherein the organic ligand is a nitrogen ligand selected from the group consisting of 2,2'-dipyridyl and 4,4'-di-tert-butyl-2,2'-dipyridyl.

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The process of Claim 48 wherein the borane is pinacolborane (BPin).

-55-

The process of Claim 48 wherein the metal catalyst is palladium.

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The process of Claim 48 wherein the metal catalyst complex is selected from the group consisting of $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}_2(\text{dba})_3$, $\text{Pd}_2(\text{dba})_3/\text{P}(\text{tBu})_3$, $\text{PdCl}_2(\text{dppf})$, and $\text{Pd}(\text{OAc})_2/\text{Cy}_3\text{P}$ wherein P is phosphorus and Ph is phenyl, dba is dibenzylideneacetone, tBu is tert-butyl, dppf is diphenylphosphinoferrocene.

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The process of Claim 48 wherein the aryl compound has the formula (R)Ar(X), the arylboronic ester has the formula (R)Ar(X)B(OR₁), and the aminoarylboronic ester has the formula
5 (R)Ar(NR₂R₃)B(OR₁)₂ wherein R, R₂, and R₃ are each selected from the group consisting of alkyl, aryl, vinyl, alkoxy, carboxylic esters, amides, and halogen; Ar is selected from the group consisting of phenyl, naphthyl, anthracyl, and heteroaryl; X is selected
10 from the group consisting of chloro, bromo, iodo, triflates, and nonaflates; and R₁ is selected from the group consisting of alkyl, hydrogen, and aryl.

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The process of Claim 48 wherein the molar ratio of the aryl compound to the borane is between about 10 to 1 and 1 to 10.

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The process of Claim 48 wherein the molar ratio of the aryl compound to borane is about 1 to 2.

-60-

The process of Claim 48 wherein the amination includes a base and a second organic ligand.

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The process of Claim 60 wherein the base is K₃PO₄.

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The process of Claim 60 wherein the second organic ligand is selected from the group consisting of PtBu_3 , 2-(N,N'-dimethylamino)-2'-dicyclophosphino-1,1'-biphenyl, 2-dicyclohexylphosphino-1,1'-biphenyl,
5 and 2-di-t-butylphosphino-1,1'-biphenyl.

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A process for producing an aminoarylboronic ester which comprises:

reacting an arylboronic ester with an organic compound containing an amine moiety in the
5 presence of a catalytically effective amount of a metal catalyst complex under anhydrous conditions wherein the organic compound is coupled to the aryl group of the arylboronic ester compound to produce the aminoarylboronic ester.

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The process of Claim 63 wherein the borane of the arylboronic ester is pinacolborane (BPin).

-65-

The process of Claim 63 wherein the metal catalyst is palladium.

-66-

The process of Claim 63 wherein the metal catalyst complex is selected from the group consisting of $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}_2(\text{dba})_3$, $\text{Pd}_2(\text{dba})_3/\text{P}(\text{tBu})_3$, $\text{PdCl}_2(\text{dppf})$, and $\text{Pd}(\text{OAc})_2/\text{Cy}_3\text{P}$ wherein P is phosphorus and Ph is
5 phenyl, dba is dibenzylideneacetone, tBu is tert-butyl, dppf is diphenylphosphinoferrocene.

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The process of Claim 63 wherein the arylboronic ester has the formula $(\text{R})\text{Ar}(\text{X})\text{B}(\text{OR}_1)$ and the aminoarylboronic ester has the formula $(\text{R})\text{Ar}(\text{NR}_2\text{R}_3)\text{B}(\text{OR}_1)_2$ wherein R, R_2 , and R_3 are each
5 selected from the group consisting of alkyl, aryl, vinyl, alkoxy, carboxylic esters, amides, and halogen; Ar is selected from the group consisting of phenyl, naphthyl, anthracyl, and heteroaryl; X is selected from the group consisting of chloro, bromo, iodo,
10 triflates, and nonaflates; and R_1 is selected from the group consisting of alkyl, hydrogen, and aryl.

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The process of Claim 63 wherein the aminoarylboronic ester is reacted with an oxidizing compound to replace the boronic ester group with an oxygen.

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The process of Claim 63 wherein the reaction includes a base and a second organic ligand.

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The process of Claim 69 wherein the base is K_3PO_4 .

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The process of Claim 69 wherein the second organic ligand is selected from the group consisting of $PtBu_3$, 2-(N,N'-dimethylamino)-2'-dicyclophosphino-1,1'-biphenyl, 2-dicyclohexylphosphino-1,1'-biphenyl,
5 and 2-di-t-butylphosphino-1,1'-biphenyl.

A process for producing a substituted phenol amine which comprises:

(a) reacting in a reaction vessel an aryl compound with a borane selected from the group consisting of a borane with a B-H, B-B, and B-Si bond in the presence of a catalytically effective amount of an iridium or rhodium complex with three or more substituents, and an organic ligand selected from the group consisting of phosphorus, carbon, nitrogen, oxygen, and sulfur organic ligands under anhydrous conditions to produce an arylboronic ester;

(b) aminating the arylboronic ester formed in the reaction vessel with an organic compound containing an amine moiety in the presence of a catalytically effective amount of a metal catalyst complex under anhydrous conditions wherein the organic compound is coupled to the aryl group of the arylboronic ester compound to produce an aminoarylboronic ester; and

(c) oxidizing the aminoarylboronic ester with a hydrogenating oxidizing compound to produce the substituted phenol amine.

The process of Claim 72 wherein the oxidizing compound is a peroxy compound selected from the group consisting of peroxymonosulfuric acid and salts thereof.

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The process of Claim 72 wherein the oxidizing compound is an alkali metal peroxymonosulfate.

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The process of Claim 74 wherein the alkali metal peroxymonosulfate is potassium peroxymonosulfate.

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The process of Claim 72 wherein the oxidizing compound is $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$.

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The process of Claim 72 wherein the oxidizing compound is an organic peroxide.

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The process of Claim 72 wherein the oxidizing compound is hydrogen peroxide.

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The process of Claim 72 wherein the iridium complex is selected from the group consisting of

$((\text{COD})\text{Ir}(\text{OCH}_3))_2$, $(\text{Cp}^*)\text{Ir}(\text{H})_2(\text{Me}_3\text{P})$,
 $(\text{Cp}^*)\text{Ir}(\text{H})(\text{BPin})(\text{Me}_3\text{P})$, $(\text{Cp}^*)\text{Ir}(\text{H})(\text{C}_6\text{H}_5)(\text{Me}_3\text{P})$,
5 $(\text{Ind})\text{Ir}(\text{COD})$, $(\text{Ind})\text{Ir}(\text{dppe})$, $(\text{MesH})\text{Ir}(\text{BPin})(\text{B}(\text{OR})_2)_2$,
 $((\text{R}_1)_3\text{P})_3\text{Ir}(\text{B}(\text{OR}_2)_2)_3$, $(\text{R}_1)_2\text{P})_2\text{Ir}(\text{BPin})_3$,
 $((\text{R}_1)_2\text{P})_3\text{Ir}((\text{R}_2\text{O})_2\text{B})_3)_2$, $((\text{R}_1)_3\text{P})_4\text{Ir}(\text{BPin})$,
 $((\text{R}_1)_3\text{P})_2\text{Ir}(\text{BPin})_3$, $(\text{MesH})\text{Ir}(\text{BPin})_3$, and $(\text{IrCl}(\text{COD}))_2$,
 $(\text{PMe}_3)_2\text{IrH}_5$, $((\text{R}_1)_3\text{P})_2\text{IrH}_5$, and $((\text{R})_3\text{P})_2\text{IrH}_x(\text{B}(\text{OR}_2)_2)_{5-x}$
10 where x is 0-4, wherein Cp^* is 1,2,3,4,5-pentamethylcyclopentadienyl, BPin is pinacolborane, Me is methyl, H is hydrogen, P is phosphorus, Ind is indenyl, COD is 1,5-cyclooctadiene, MesH is mesitylene, and wherein R, R_1 , and R_2 are hydrogen,
15 linear or branched alkyl containing 1 to 8 carbons, aryl, or a carbon in a cyclic structure.

-80-

The process of Claim 72 wherein the iridium complex is $(\text{Ind})\text{Ir}(\text{COD})$ wherein Ind is indenyl and COD is 1,5-cyclooctadiene.

-81-

The process of Claim 72 wherein the iridium complex is $((\text{COD})\text{Ir}(\text{OCH}_3))_2$ wherein COD is 1,5-cyclooctadiene.

-82-

The process of Claim 72 wherein the organic ligand is a phosphorus organic ligand selected from the group consisting of trimethyl phosphine (PMe_3), 1,2-bis(dimethylphosphino)ethane (dmpe), and 1,2-bis(diphenylphosphino)ethane (dppe).

-83-

The process of Claim 72 wherein the organic ligand is a nitrogen ligand selected from the group consisting of 2,2'-dipyridyl and 4,4'-di-tert-butyl-2,2'-dipyridyl.

-84-

The process of Claim 72 wherein the borane is pinacolborane (BPin).

-85-

The process of Claim 72 wherein the metal catalyst is palladium.

-86-

The process of Claim 72 wherein the metal catalyst complex is selected from the group consisting of $\text{Pd}(\text{PPh}_3)_4$, $\text{Pd}_2(\text{dba})_3$, $\text{Pd}_2(\text{dba})_3/\text{P}(\text{tBu})_3$, $\text{PdCl}_2(\text{dppf})$, and $\text{Pd}(\text{OAc})_2/\text{Cy}_3\text{P}$ wherein P is phosphorus and Ph is phenyl, dba is dibenzylideneacetone, tBu is tert-butyl, dppf is diphenylphosphinoferrocene.

-87-

The process of Claim 72 wherein the aryl compound has the formula $(R)Ar(X)$, the arylboronic ester has the formula $(R)Ar(X)B(OR_1)$, and the aminoarylboronic ester has the formula
5 $(R)Ar(NR_2R_3)B(OR_1)_2$ wherein R, R_2 , and R_3 are each selected from the group consisting of alkyl, aryl, vinyl, alkoxy, carboxylic esters, amides, and halogen; Ar is selected from the group consisting of phenyl, naphthyl, anthracyl, and heteroaryl; X is selected
10 from the group consisting of chloro, bromo, iodo, triflates, and nonaflates; and R_1 is selected from the group consisting of alkyl, hydrogen, and aryl.

-88-

The process of Claim 72 wherein the molar ratio of the aryl compound to the borane is between about 10 to 1 and 1 to 10.

-89-

The process of Claim 72 wherein the molar ratio of the aryl compound to borane is about 1 to 2.

-90-

The process of Claim 72 wherein the amination includes a base and a second organic ligand.

-91-

The process of Claim 90 wherein the base is K_3PO_4 .

The process of Claim 90 wherein the second organic ligand is selected from the group consisting of PtBu_3 , 2-(N,N'-dimethylamino)-2'-dicyclophosphino-1,1'-biphenyl, 2-dicyclohexylphosphino-1,1'-biphenyl,
5 and 2-di-t-butylphosphino-1,1'-bipheyl.